In_2S_3-bonded laccase as photoelectrode for H_2O oxidation to O_2

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Abstract

We showed earlier photocatalytic H_2 generation irradiating a hydrogenase-In_2S_3 combination.[1a] We report now recent results1[b] of photoelectrochemical evolution of O_2 from water using as light absorber In_2S_3, a semiconductor with bandgap E_g=2.0 eV capable of photocatalysis with λ<650 nm light,[2a] and as co-catalyst the enzyme *Trametes Laccase* (ThLc), able to electrochemically oxidize water to O_2[3] (Fig. 1a).

In_2S_3 powder was laid on a FTO electrode and ThLc was bonded to it via aminophenyl groups. An O_2 sensor located near the electrode could detect O_2 (without simultaneous production of H_2O_2) during voltammograms when irradiated in aqueous solution buffered at pH=7.1 (Fig. 1b); control tests showed that In_2S_3, light and covalently bonded ThLc were all needed for O_2 formation. Overpotential decrease by >0.7 V was found, and calibration of the O_2 sensor evidenced faradaic efficiencies of 45% (some photo-corrosion probably occurred). This is the first time that enzyme-catalyzed O_2 formation is seen upon visible light irradiation of a semiconductor, and shows high promise since V-doped In_2S_3 has shown ability to couple two low energy photons to achieve a photocatalytically active higher energy electron excitation,2[b] like in photosynthesis Z-scheme.

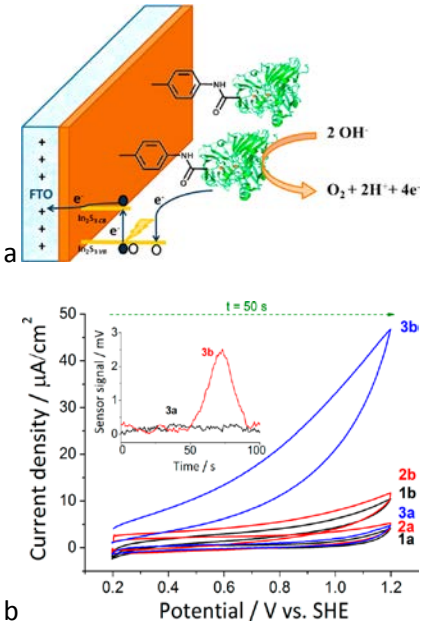

Fig. 1 a) Photoelectrochemical setup b) O_2 formation (inset) in cyclic voltammogram (3b) with this setup

[1] a) C. Tapia *et al.* ACS Catal. 6 (2016) 5691; b) *ibid.* ACS Catal. 7 (2017) 4881.
[2] a) R. Lucena *et al.,* Catal. Commun. 20 (2012) 1; b) *ibid.* J. Mater. Chem. A 2 (2014) 8236
[3] M. Pita *et al.* J. Am. Chem. Soc. 136 (2014) 5892.